catalyst was filtered and the alcohol removed by distillation. Upon vacuum distillation, 33 g. of a colorless liquid, b.p. 135–136° (0.85 mm.), n^{25}D 1.4503, was collected.

Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84. Found: C, 64.29; H, 11.88.

The constants for the other saturated ethers are listed in Table III.

The infrared spectra of all of the saturated ethers of glycerol were similar to the spectra of the 1-alkenyl ethers except for the absence of the absorption bands at 6, 8.6, and 10.7 μ, which is in agreement with the saturated structure.

The saturated ethers of glycerol gave a positive periodic acid test substantiating the α-position of the 1-alkenyl ether linkage on the glycerol moiety.

The saturated ether, 3-octyloxy-1,2-propanediol, was alternatively synthesized by refluxing the sodium salt of isopropylidene glycerol with octyl bromide to form the octyl ether. The ketal linkage was cleaved by acid hydrolysis, and the product was distilled to yield a colorless liquid, boiling at 130° (0.65 mm.); n^{28}D 1.4490. The boiling points and refractive indexes of the two saturated ethers indicate that the compounds are identical and, therefore, substantiate the proposed structure of the 1-alkenyl ether.

Saturated Ether of Trimethylene Glycol.—A hydrogenation, similar to that previously mentioned, was carried out on 3-(1-heptenyloxy)-1-propanol to yield 3-heptyloxy-1-propanol. The product was a colorless liquid recovered by distillation, b.p. 75–75.5° (0.08 mm.); $n^{24.5}$D 1.4385.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.86; H, 12.72. Found: C, 69.42; H, 12.01.

Derivatives of Dicyanamide[1]

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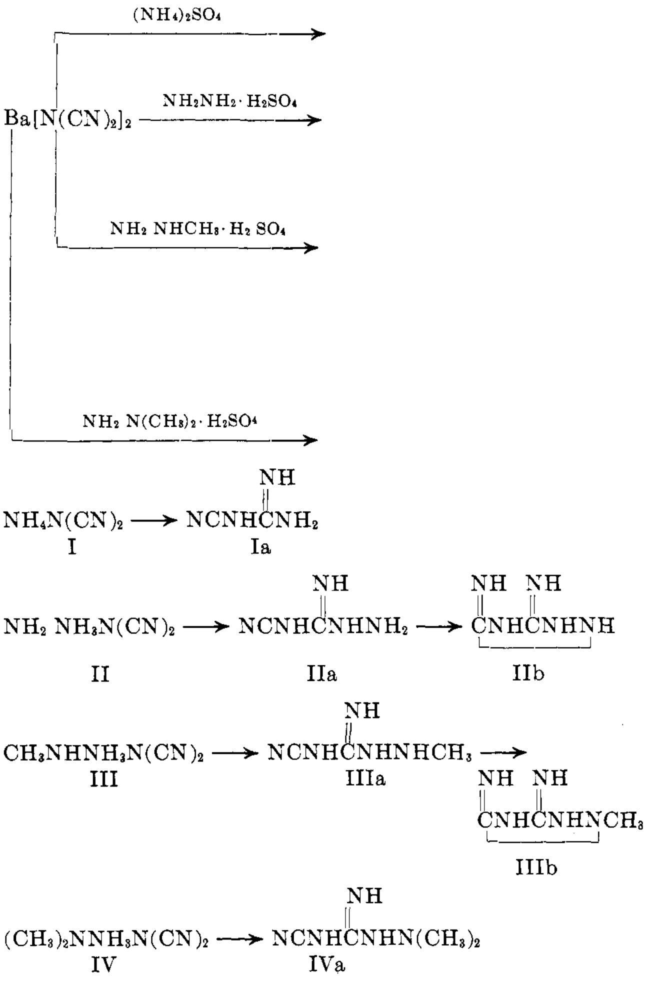
The reaction of barium dicyanamide with the sulfate salts of ammonia, hydrazine, N-methylhydrazine, and N,N-dimethylhydrazine was investigated. Infrared spectroscopy was used to establish whether the reaction products were the salts of dicyanamide or the rearranged products. The preparation and characterization of ammonium and hydrazine dicyanamide is reported. The latter compound was found to be thermally unstable, and its rate of decomposition was determined.

In our study of N-cyano compounds, it was of interest to prepare and characterize the ammonium and hydrazine salts of dicyanamide, $HN(CN)_2$. American Cyanamide Company has prepared[2] a variety of aliphatic amine salts of dicyanamide by treating calcium dicyanamide with the amine sulfate; some aliphatic amine salts of dicyanamide rearrange spontaneously to substituted dicyanamides at room temperature, while others are quite stable and frequently require the application of considerable amount of heat in order to effect this rearrangement.

The reaction of barium dicyanamide with the sulfate salts, of ammonia, hydrazine, N-methylhydrazine, and N,N-dimethylhydrazine was investigated in this laboratory to determine whether the reaction products were the salts of dicyanamide or the rearranged materials as shown in Chart I. It was expected that the initial products of these reactions would be ammonium dicyanamide (I), hydrazine dicyanamide (II), N-methylhydrazine dicyanamide (III), and N,N-dimethylhydrazine dicyanamide (IV). These salts might be stable or might rearrange to N-cyanoguanidine (Ia), N-cyano-N′-aminoguanidine (IIa), N-cyano-N′-methylaminoguanidine (IIIa), and N-cyano-N′-dimethylaminoguanidine (IVa), respectively. Compounds IIa and IIIa could rearrange further by cyclizing to give guanazole (IIb) and methylguanazole (IIIb). Since the salts and the rearrangements products are isomeric and would have the same empirical formula and similar physical properties, it would be necessary to find a method to distinguish unequivocally between them. Infrared spectroscopy, *via* the potassium bromide pellet technique, seemed to offer the best method for the identification of the products. The salts I–IV should exhibit the strong absorption of C≡N; the rearranged cyanoguanidines Ia–IVa would have the characteristic absorption of both C≡N and C=N; while the cyclic compounds IIb and IIIb would have only the C=N vibration.

CHART I



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[1] Presented before the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

[2] "Cyanamide New Product Bulletin," Coll. Vol. II, December, 1950.

The general procedure for conducting these reactions was to treat an aqueous solution of barium dicyanamide with the amine sulfate. This caused an immediate precipitation of barium sulfate. After filtering off the solid, the aqueous solution was concentrated *in vacuo*, generally at ambient temperature, to give the product.

Initial work was directed to the synthesis of ammonium dicyanamide (I). The aqueous solution was concentrated at 30° (1 mm.) to give a crystalline solid which melted at 131°, resolidified immediately, remelted at 215°, resolidified at about 250°, and then did not melt up to 400°. The elemental analysis of the product corresponded to the desired $C_2H_4N_4$. The infrared spectrum (Fig. 1) showed three bands in the C≡N region near 2155, 2220, and 2260 cm.$^{-1}$ and a very weak absorption at 1630 cm.$^{-1}$.[3] The intensity ratios of the three peaks in the C≡N region were compared with the spectra of the silver, barium, and lithium salts of dicyanamide prepared in these laboratories and were found to be nearly identical (Table I). All of these spectra are very similar to those reported for the sodium and lead salts of dicyanamide.[4] The spectrum of N-cyanoguanidine (Fig. 1) shows strong doublets near 2200 and 1630 cm.$^{-1}$, and is thus quite different from the reaction product. Furthermore, treatment of the reaction product with silver nitrate gave a silver salt whose infrared spectrum was identical to that of pure silver dicyanamide. Therefore, it was concluded that the structure of the reaction product was I and not Ia.

Table 1

Summary of Intensities of Characteristic C=N and C≡N Valence Vibrations

Compound	Molar absorptivity ϵ_{1630} (C=N) 10^5 g./mole-cm.	Molar absorptivity ϵ_{2155} (C≡N) 10^5 g./mole-cm.	Ratio of C≡N intensities $\frac{\epsilon_{2155}}{\epsilon_{2155}}$	Ratio of C≡N intensities $\frac{\epsilon_{2220}}{\epsilon_{2155}}$	Ratio of C≡N intensities $\frac{\epsilon_{2260}}{\epsilon_{2155}}$
$AgN(CN)_2$	[a]	13.45	1.00	0.40	0.68
$Ba(N(CN)_2)_2$	[a]	3.84	1.00	0.49	0.61
$NH_4N(CN)_2$	[a]	3.52	1.00	0.49	0.58
$NH_2NH_3N(CN)_2$	1.01	4.83	1.00	0.44	0.58
$\underline{\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNH}$	3.83	[a]		[a]	
$\underline{\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNCH_3}$	1.75	[a]		[a]	
$NCNH\overset{NH}{\overset{\|}{C}}NHN(CH_3)_2$	1.15[b]	1.24[d]		[a]	
$NCNH\overset{NH}{\overset{\|}{C}}NH_2$	3.69[c]	3.49[e]		[a]	

[a] Not applicable. [b] Average of absorbances at 1615 and 1645 cm.$^{-1}$. [c] Measured at 1635 cm.$^{-1}$. [d] Measured at 2182 cm.$^{-1}$. [e] Measured at 2162 cm.$^{-1}$.

The foregoing procedure for the preparation of I was found to be more satisfactory than those reported in the literature. Madelung and Kern[5] reported that when an ammonium solution of cupric dicyanamide was treated with hydrogen sulfide, cupric sulfide was precipitated. After boiling the filtrate, they reported that I was isolated from the filtrate as white needles, m.p. 116°. American Cyanamide Company reported[2] that I was readily prepared by stirring an aqueous mixtu e of zinc dicyanamide and ammonium hydroxide.

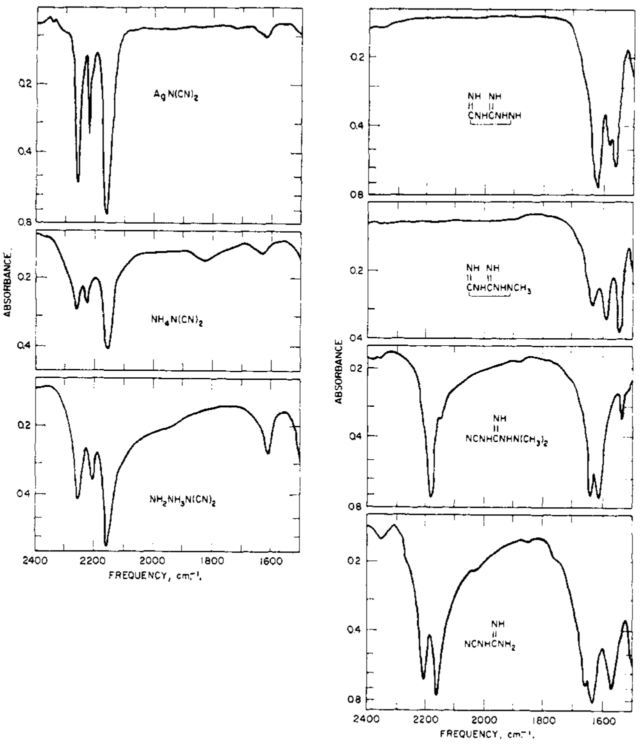
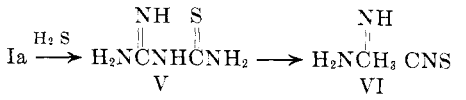


Fig. 1.—Infrared spectrum of dicyanamide derivatives in the C≡N and C=N regions. Concentrations of pellets (10^{-5} moles/g.):
$AgN(CN)_2$ (0.49); $NH_4N(CN)_2$ (0.95); $NH_2NH_3N(CN)_2$ (1.07); $\underline{\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNH}$ (1.62); $\underline{\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNCH_3}$ (0.88); $NCNH\overset{NH}{\overset{\|}{C}}NHN(CH_3)_2$ (4.45); $NCNH\overset{NH}{\overset{\|}{C}}NH_2$ (1.79).

In repeating the work of Madelung and Kern,[5] the ammonium solution of cupric dicyanamide was treated with hydrogen sulfide for thirty minutes and worked up in the designated manner. The product was isolated as white needles, m.p. 100–116°; two recrystallizations from ethanol raised the melting point to 129–140°. Elemental analysis did not correspond to I but rather to a compound with the empirical formula of $C_2H_6N_4S$. The infrared spectrum showed a doublet at 2155 and 2210 cm.$^{-1}$, and a strong absorption at 1630 cm.$^{-1}$. It has been reported that N-cyanoguanidine (Ia) reacts with hydrogen sulfide in the presence of aqueous ammonia to yield guanylthiourea (V),[6] and that V on heating is converted to the isomeric guanidine thiocyanic acid (VI).[7] This evidence indicates that the reaction product is probably a mixture of V and VI.



$$\text{Ia} \xrightarrow{H_2S} \underset{\text{V}}{H_2N\overset{NH}{\overset{\|}{C}}NH\overset{S}{\overset{\|}{C}}NH_2} \longrightarrow \underset{\text{VI}}{H_2N\overset{NH}{\overset{\|}{C}}H_3\ CNS}$$

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[3] The 1630-cm.$^{-1}$ band is probably due to water rather than C=N absorption, since a small absorption in this region due to water in the potassium bromide pellet is very difficult to avoid. It will be noted that this same band does appear in the silver dicyanamide spectrum where presumably no C=N is present. Further, the shape of the 1630-cm.$^{-1}$ band in the ammonium dicyanamide is broad in contrast to its sharpness in compounds in the series where the C=N is known to be present.

[4] M. Kuhn and R. Mecke, *Ber.*, **94**, 3010 (1961).

[5] W. Madelung and E. Kern, *Ann.*, **427**, 1 (1922).

[6] E. Bamberger, *Ber.*, **16**, 1459 (1883).

[7] B. Rathke, *ibid.*, **11**, 962 (1878).

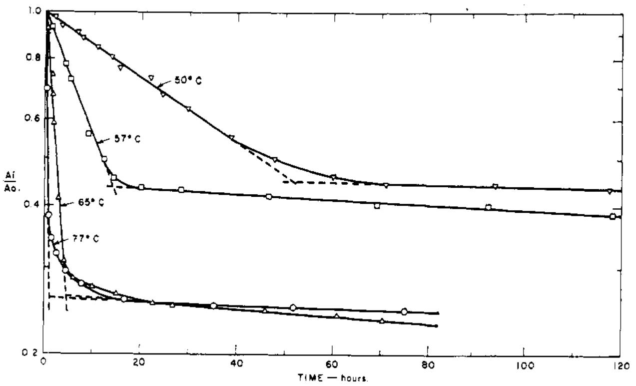

Fig. 2.—Relative absorbance of the C≡N vibration at 2155 cm.$^{-1}$ of hydrazine dicyanamide as a function of time and temperature.

Procedure of Madelung and Kern[5] was repeated in which the ammonium solution of cupric dicyanamide was treated with hydrogen sulfide for only five minutes. In this case ammonium dicyanamide was isolated as evidenced by the fact that the infrared spectrum of the product was identical to that of I prepared from barium dicyanamide and ammonium sulfate. Using the American Cyanamide procedure[2] for the preparation of I, a product was obtained whose elemental analysis indicated it to be a mixture of the ammonium and zinc salts of dicyanamide.

The aqueous solution from the reaction of barium dicyanamide and hydrazine sulfate was concentrated at 50° (1 mm.) to give a white crystalline solid, m.p. 211–212°. The elemental analysis of the product corresponded to the desired empirical formula of $C_2H_5N_5$, but the infrared spectrum did not show any of the characteristic absorption for C≡N near 2200 cm.$^{-1}$, but a strong doublet near 1630 cm.$^{-1}$, characteristic of the cyclic C=N stretching vibration.[8–10] These results indicated that the material isolated was guanazole (IIb). The identity of the product was confirmed as IIb since a mixture melting point with an authentic sample was not depressed, and the infrared spectra were the same. In the concentration of the aqueous solution at 50° (1 mm.), when the product started to crystallize, it was noticed that considerable heat was evolved. This was particularly evident in the larger runs which were made. This highly exothermic reaction is undoubtedly caused by the isomerization of II to IIb. In one run, in which the aqueous solution was concentrated at 60–70° (1 mm.), the product crystallized and then decomposed with explosive violence.

When the aqueous solution from the reaction of barium dicyanamide and hydrazine sulfate was concentrated at 20° (1 mm.), a solid melting at 97–97.5° was obtained. This material resolidified at 105° and then remelted at 211–212°. The high melting material was identical to IIb. Elemental analysis of the low melting product corresponded again to $C_2H_5N_5$. The infrared spectrum of this product showed three bands near 2155, 2220, and 2260 cm.$^{-1}$ and a moderate absorption at 1630 cm.$^{-1}$ (Fig. 1). Similar absorptions were obtained when the infrared spectrum was determined in solution or in mull. The intensity ratio of the three bands in the C≡N region was essentially the same as recorded for the salts of dicyanamide (Table I). Treatment of this reaction product with silver nitrate gave a silver salt whose infrared spectrum was identical to that of pure silver dicyanamide. On the basis of this evidence it was concluded that the low melting product was hydrazine dicyanamide (II).

In the course of this work, it was noted that the infrared spectra of II changed very slowly at ambient temperature in a dry atmosphere. After six weeks the apparent molar absorptivity in the C≡N region had dropped from 4.83 to 2.83 (10^5 g./mole-cm.), and absorption in the C=N had increased from 1.01 to 3.56 (10^5 g./mole-cm.). A quantitative evaluation of the thermal decomposition of II was undertaken. If the thermal decomposition follows first-order reaction kinetics, the following equation results

$$\log \frac{A_i}{A_0} = -\frac{k}{2.303}\,t \qquad (1)$$

where A_i is the absorbance of the C≡N vibration at 2155 cm.$^{-1}$ at any time t, and A_0 is the absorbance when $t = 0$, and k is the specific reaction rate. Plots of log A_i/A_0 as a function of time and temperature (Fig. 2) reveal that the decomposition follows a first-order reaction mechanism initially, then abruptly slows down. This indicates that further decomposition occurs and is controlled by a different mechanism. It is interesting to note that at different temperatures the second, slow reaction does not assume control at the same degree of decomposition. This fact implies the competing reaction has an induction period which is temperature dependent. When the specific reaction rate of the first step of decomposition, determined by equation 1 from the slope of the curves of Fig. 2, is plotted as a function of the reciprocal of the absolute temperature, a straight line is obtained. The Arrhenius plot shows the initial decomposition reaction has an activation energy of 41.9 kcal./mole.

The product of the aqueous reaction of monomethylhydrazine sulfate with barium dicyanamide had an infrared spectrum (Fig. 1) similar to that obtained for guanazole (IIb) and was assigned the structure IIIb. It was not possible to isolate the intermediates III or IIIa.

The product of the aqueous reaction of 1,1-dimethylhydrazine sulfate with barium dicyanamide had an infrared spectrum similar to that of cyanoguanidine (Ia) and was assigned the structure IVa. The results are summarized in Table II.

Experimental

Chemical Analyses.—Microanalyses were by Berkeley Analytical Laboratory, Berkeley, California. Melting points are uncorrected. The dicyanamide content of the barium dicyanamide was determined by a modified Volhard technique after removal of any free cyanide ions.[11] The barium content of these stock solutions was determined by photometric titration with disodium ethylenediamine tetraacetate using Eriochrome Black T as indicator.[12]

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[8] E. Lieber, D. R. Levering, and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

[9] P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, **76**, 5169 (1954).

[10] H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand and Company, New York, N. Y., 1949.

[11] Private communication, American Cyanamide Co.

[12] K. Rowley, R. W. Stoenner, and L. Gordon, *Anal. Chem.*, **28**, 136 (1956).

TABLE II

DERIVATIVES OF DICYANAMIDE

Compound	Yield, %	M.p., °C.	Recryst.	Formula	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$NH_4\ N(CN)_2$	79.8	131[a]	Methanol–ether	$C_2H_4N_4$	28.57	4.79	66.64	28.40	4.73	66.72
$NH_2\ NH_3N(CN)_2$	61.6	97–97.5	95% Ethanol–ether	$C_2H_5N_5$	24.24	5.09	70.68	23.99	4.94	70.36
 $\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNH$	81.3	211–212	95% Ethanol	$C_2H_5N_5$	24.24	5.09	70.68	24.46	5.07	70.60
 $\overset{NH}{\overset{\|}{C}}NH\overset{NH}{\overset{\|}{C}}NHNCH_3$	35.8	157–159	Methanol–ether	$C_3H_7N_5$	31.85	6.24	61.91	31.84	6.18	62.06
 $NCNH\overset{NH}{\overset{\|}{C}}NHN(CH_3)_2$	40.1	214–215	95% Ethanol	$C_4H_9N_5$	37.78	7.13	55.09	37.78	7.02	54.58

[a] Resolidifies immediately, remelts at 215°, and resolidifies at 250°.

Infrared Analyses.—All infrared spectra were obtained on a Perkin-Elmer Model 221 infrared spectrometer equipped with a prism-grating interchange. Samples were prepared by standard potassium bromide pellet technique[13,14] in which approximately 350 mg. of carefully prepared mixture is pressed in a 12.7-mm. die. The mixture is prepared by transferring a weighed portion of finely divided sample together with 1 g. of spectroscopic grade potassium bromide into a polystyrene mixing container and intimately mixing these ingredients for 60 sec. in a Wig-L-Bug agitator.

Absorbances of vibration modes were determined by the baseline method[15,16]; molar absorptivities, ϵ_i, of these vibrations were calculated from the following

$$\epsilon_i = \frac{A_i A_p d}{W_p C}$$

where A_i = absorbance of vibration i
A_p = area of the pellet
d = density of the pellet assumed to be equal to that of potassium bromide 2.75 g./cm.^{3}
W_p = weight of pellet
C = concentration of sample in pellet moles/g.

Thermal Decomposition Studies.—Potassium bromide pellets of freshly prepared II were made and maintained at 77°, 65°, 57°, and 50°. Periodically these pellets were removed from the constant temperature environment and their spectra obtained. It was assumed that the time required for the pellet to cool to room temperature was identical to that required for the pellet to attain the desired temperature after the spectrum had been obtained, and the decomposition at room temperature was negligible during the interval required to obtain the spectrum. Possible catalytic effects of potassium bromide were ruled out by agreement of periodic checks of the spectrum of a freshly prepared pellet made from II which had been stored at elevated temperature with that of the pellet stored at the same temperature.

Barium Dicyanamide.—To a solution of 946.5 g. (3.0 moles) of barium hydroxide octahydrate in 10 l. of distilled water was added 678.3 g. (3.0 moles) of zinc dicyanamide.[17] The reaction mixture was stirred under nitrogen for 16 hr. and then filtered to remove the precipitated zinc hydroxide. The colorless aqueous filtrate weighed 10,600 g. Analysis of the solution for the dicyanamide ion showed 0.542 mmole of dicyanamide ion per gram of solution. This corresponded to a yield of 5.75 moles (95.7%) of barium dicyanamide. The stock solution of barium dicyanamide was used directly for the subsequent reactions.

Ammonium Dicyanamide (I).—To a solution of 13.45 g. (0.05 mole) of barium dicyanamide in 50 ml. of water was added a solution of 6.65 g. (0.05 mole) of ammonium sulfate in 20 ml. of water. Barium sulfate immediately precipitated. The reaction mixture was stirred for 10 min. and filtered through Celite on a Büchner funnel. The filtrate was concentrated on a Rinco evaporator at 30° (1 mm.), leaving 6.7 g. (79.8%) of white needles.

Guanylthiourea (V).—To a slurry of 4.89 g. (0.025 mole) of cupric dicyanamide and 10 ml. of water was added 50 ml. of ammonium hydroxide. The salt dissolved giving a deep blue solution. Hydrogen sulfide gas was bubbled through the solution for 30 min. The black precipitate of cupric sulfide was filtered leaving a deep yellow solution. The solution was boiled causing additional solid to separate. Filtration with the aid of Celite gave a colorless solution which was concentrated *in vacuo* leaving 2.3 g. (39.0%) of white solid, m.p. 100–116°. Two recrystallizations from ethanol gave white needles, m.p. 129–140°.

Anal. Calcd. for $C_2H_6N_4S$: C, 20.33; H, 5.09; N, 47.45. Found: C, 19.92; H, 4.65; N, 47.60.

Hydrazine Dicyanamide (II).—To a solution of 269 g. (1.0 mole) of barium dicyanamide in 2 l. of distilled water was added 70.55 ml. of 90.74% hydrazine (2.0 moles). The solution was cooled in an ice bath and 54.26 ml. (0.98 mole) of concentrated sulfuric acid was added dropwise. The reaction mixture was stirred for 15 min. and filtered to remove the barium sulfate. The filtrate was concentrated on a Rinco evaporator at 20° (1 mm.) until a viscous oil was obtained. The concentration was stopped before any product had crystallized. The oil was cooled in an ice bath and 750 ml. of isopropyl alcohol was added with stirring, causing the oil to solidify. The white needles were collected, washed with isopropyl alcohol, and dried giving 120 g. (61.6%). The crystals melted at 85–88°, resolidified at 95°, and remelted at 198–204°. The product was purified by dissolving in 95% ethanol and reprecipitating with anhydrous ether. The white needles thus obtained melted at 97–97.5°, resolidified at 105°, and remelted at 207–209°.

Guanazole (IIb).—To a solution of 5.0 g. (0.0155 mole) of barium dicyanamide in 30 ml. of distilled water was added 1.06 ml. of 90.74% hydrazine (0.031 mole). The solution was cooled in an ice bath and 0.81 ml. (0.0147 mole) of concentrated sulfuric acid was added. The reaction mixture was stirred for 15 min. and filtered. The filtrate was concentrated on a Rinco evaporator at 50° (1 mm.) leaving 2.5 g. (81.3%) of white solid, m.p. 200–208°. Recrystallization from 95% ethanol raised the melting point to 211–212°.

Acknowledgment.—The authors are indebted to the Division Research Committee of Stanford Research Institute for the financial support of this work.

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[13] M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

[14] R. S. Browning, S. E. Weberley, and F. C. Nachod, *Anal. Chem.*, **27**, 7 (1955).

[15] N. Wright, *Ind. Eng. Chem.* (*Anal. Ed.*), **13**, 1 (1941).

[16] J. J. Heigl, M. F. Bell, and J. V. White, *Anal. Chem.*, **19**, 293 (1947).

[17] Technical grade of 87.3% purity from American Cyanamide Co.